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FINAL REPORT

PART II

RADIOACTIVE OZONE GENERATOR

OZONE CHEMILUMINESCENT STUDY

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FOREWARD

This report describes the results of a program to design and construct a prototype ozone generator using a radioisotope as energy source. The work was administered by the Methods Development Branch, Chemistry and Physics Division, Bureau of Engineering and Physical Sciences, National Air Pollution Control Administration, Mr. Andrew E. O'Keeffe, Contract Officer.

This is Part II of the Final Report to Contract No. CPA-22-69-7. Part I deals with the design, construction, and testing of a feasibility model of a chemiluminescent ozone meter. This part deals with the testing of an ozone generator designed and constructed by M. Steinberg and R. N. Dietz of The Brookhaven National Laboratory.

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RADIOACTIVE OZONE GENERATOR

Final Report

INTRODUCTION AND PRELIMINARY CONSIDERATIONS

When high energy particles pass through gases, they give up their energy to the gas molecules in any of several ways. One of these is by breaking of the interatomic bonds, resulting in the formation of atoms in either ionized or neutral states. These atoms then rearrange themselves into more or less stable molecules again, which may or may not be similar to the original molecules, depending on conditions which prevail in the system.

The decay of radioactive isotopes produces high energy particles and/or gamma rays, which can cause the above phenomena. The smell of ozone was observed in the vicinity of high intensity radioactive sources soon after radioactivity was discovered. Quantitative studies (1) with alpha particles showed that the number of ozone molecules formed is directly related to the total number of ion pairs formed. It was a logical extension of these observations to predict that a stable and reproducible generator of ozone should result from passing air or oxygen over a radioisotope having a reasonably long half-life.

Initial considerations of generator design pointed up the fact that the choice of radioisotope is crucial to its success. Several properties, some mutually exclusive, are important. First, the isotope must have a long enough half-life such that the concentration of ozone produced would remain relatively constant over the useful life of the generator. On the other hand, if the isotope emits alpha particles, its half-life should be short enough, (its specific activity should be great enough) to generate the desired amount of ozone. Second, the isotope should preferably be either an alpha or a pure beta emitter. To have gamma rays associated with the decay

would necessitate heavy shielding around the device. Third, if the isotope is a beta emitter then its decay energy should be great enough to generate the desired amount of ozone without requiring an excessive quantity of isotope. Fourth, chemical properties of the isotope are important since it is necessary to deposit the isotope on a surface for exposure to oxygen or air. Cost of the isotope is also important.

A search through the isotope literature narrowed the available and potentially useful species to those listed in Table I. An attempt to

TABLE I

Isotopes for Use in Ozone Generator

Alpha Emitters	Half-Life	Cost
Po-210	138 d	$ 1/millicurie
Pu-238	86.4y	$25/millicurie
Am-241	458 y	50¢/millicurie

Beta Emitters	Half-life, years	Energy, KeV	Cost
Pm-147	2.6	220	50¢/curie
Tl-204	4.1	770	75¢/millicurie
H-3	12.5	18	$ 2/curie
Sr-90 (Y-90)	20 (61h)	610 (2.2 MeV)	50¢/curie
Pb-210 (Bi-210)	22 (5d)	18 (1.17 MeV)	
Ni-63	125	67	$ 5/millicurie
C-14	5500	155	$ 6/millicurie
Tc-99	2×10^5	290	$50/17 millicurie
Cl-36	3.1×10^5	714	35¢/microcurie

estimate the quantity of these isotopes needed to produce the desired amount of ozone was not successful. In principle, it should be possible to make such an estimate if the particle energy is known, the bond energy of the oxygen molecule is known, and if simplifying assumptions are made about the combination of oxygen atoms with oxygen molecules to form ozone. The literature

however, indicates that the calculation is not simple. Not only does radiation lead to formation of ozone, it also contributes to decomposition of the compound once formed (2). Studies in static systems (3-5) show that the decomposition mechanism is extremely complicated. In short, attempts to calculate the quantity of isotope needed were fruitless.

Initial considerations of generator design also concluded that an alpha emitter would be better than a beta emitter. This conclusion results from a knowledge that alpha particles expend their total energy in short distances in air, whereas beta particles require much greater distances. For example, 300 cm of air are required to stop completely, a 1 MeV beta particle, while only 3.2 cm of air will stop a 5 MeV alpha particle. Thus, if all of the energy available in radioactive decay were to be utilized in generating ozone, a small alpha device operating at atmospheric pressure would be conceivable, while a very large device would be required for beta emitters, unless it were operated at high pressure.

The choice of alpha emitters is very limited, as shown in Table I. Polonium-210 has an unfortunately short half-life, although it is readily available and the technology for its incorporation into radiation devices is well developed. Plutonium-238 is available and has a very satisfactory half-life, but because of its cost--and possible licensing problems--it was given only little consideration. Americium-241 was investigated at some length. Although the half-life borders on the too-long side (its specific activity is almost too low leading to self-absorption problems), its availability and cost recommend it. After considerable inquiry among possible fabricators of an Americium-241 source, however, it became clear that no vendor would guarantee the integrity of any alpha source longer than three or four months after preparation. Such a guarantee is absolutely essential, because alpha emitters are so hazardous in the body. Under

certain circumstances, the supplier of Po-210 sources would guarantee integrity of his product, but because of its short half-life, Po-210 was not further considered. Alpha emitters were thus ruled out as a source of energy in the ozone generator.

The alternative of using a beta emitter became necessary. But unless a weak (in energy) source were used, the physical size of the proposed generator would be unacceptable. Table I shows that only H-3 and Ni-63 have beta energies less than 100 KeV. Both have satisfactory half-lives. Unfortunately, however, the technology of preparing relatively high intensity tritium sources in planar configuration is not well developed. And also unfortunately, whereas Ni-63 would be ideal and nickel plating is easy, the cost of the estimated 1 to 10 curies of Ni-63 is prohibitive.

The possibility of pressurizing the generator was then presented. The technology of large scale, high-pressure Sr-90 ozone generators had already been developed for commercial purposes (6). It was thought that a small device based on this work could be built. After extensive discussion and consideration, the decision was made to proceed with design and construction of a Sr-90 ozone generator. Permission was obtained from the Atomic Energy Commission for Brookhaven National Laboratory to build the first model.

DESCRIPTION OF THE SR-90 OZONE GENERATOR

The ozone generator is an approximately spherical vessel, 2.5 inches in diameter, in which is fitted a stainless steel needle containing 0.5 curies of Sr-90. The vessel is protected both for pressure and radiation. (A complete physical description of the device is given in the instruction manual--BNL-14199--prepared by M. Steinberg and R. N. Dietz, which forms an Appendix to this report.) Dry oxygen at several atmospheres pressure is

passed through the vessel and exits through one of four orifices. The orifices control the flow rate of oxygen through the vessel, thereby controlling residence time of the gas in vicinity of the Sr-90, which in turn determines the quantity of ozone formed.

Operation of the generator is simple: tank oxygen is introduced in the inlet at the desired pressure. A stainless steel tube and fitting is attached at that orifice which will give the desired flow rate and ozone concentration. After a period of time the generator produces a steady output of ozone. Details of the pressure/flow-rate/ozone concentration/time relationships are involved and were studied at length both at Brookhaven National Laboratory and here at R.T.I. These are discussed in the following paragraphs.

CHARACTERISTICS OF THE GENERATOR

A. Moisture Content of Oxygen

Section 2.2.4 of the BNL report (Appendix) states that moisture content of the oxygen is very important. This has been confirmed. Although it was not possible to study the effect as extensively as was done by BNL, we did find that oxygen which had been passed through a dry-ice/acetone moisture trap produced more than twice as much ozone as did oxygen, from the same supply tank, which had not been cooled (Table II). Other variables in the experiment were kept identical.

TABLE II

Effect of Moisture on Ozone Production

	Tank Oxygen	Dry Oxygen
Ozone, ppb	132	313

The temperature of a dry-ice/acetone mixture is -81°C at which the vapor pressure of ice is 0.00034 mm. This corresponds to a water vapor

concentration in air of about 0.3 ppm. All experiments were thus carried out using the dry-ice/acetone trap to assure reproducibility between different tanks of oxygen and to maximize ozone concentrations.

B. Pressure-Flow Rate Relations

According to the BNL report, the flow rate of gas from any orifice is proportional to the pressure applied. It is not a linear function, however, but increases slightly faster than linear (i.e. the flow rate from an orifice at 2 P atmospheres is slightly more than twice the flow rate at P atmospheres). The BNL report also tabulates, in Fig. 6, multipliers to be used for the various orifices.

We have not confirmed the multipliers for orifices 2 and 3. We also find a lower concentration of ozone from orifice 1 than reported by BNL and a higher concentration from orifice 2. These are discussed in detail in this report. Characteristics of the Generator, Section D, Orifice 4 has such a high flow rate and such a low ozone concentration that it was not investigated.

We differ with the BNL report, also, in magnitude of flow rate values. Table III gives values for orifice 1 found at RTI and those taken from the report. Table IV gives flow rates from three orifices found at RTI.

TABLE III

Flow Rates of Gas From Orifice No. 1

Pressure, PSI	Flow Rate ml/min	
	RTI	BNL
200	65	90
300	118	140
400	164	200
500	189	260
600	240	315
700	248	375
800	335	440

TABLE IV

Flow Rates from Orifices 1, 2 and 3

Pressure, PSI	Orifice (in ml/min)		
	1	2	3
300	118	600	5500
400	164	810	7410
500	189	1100	9410

The differences may arise from the methods of measuring pressure, although it is difficult to see how the two pressure meters could be so much different. Flow rates were measured at RTI using Hastings-Raydist mass flow meters which supposedly are accurate to plus-or-minus 2% of true rates. It was not possible to compare these with the Manostat Corp. predictability flow meters used at Brookhaven. But, for reasons to be discussed in detail in the next section, the flow rate from any given orifice is relatively unimportant: it has little effect upon ozone concentration. A knowledge of flow rate is needed only to be assured that the generator is supplying enough flow to the ozone meter being calibrated.

C. Ozone Concentration-Flow Rate Relations

The simple picture of ozone production by means of energy deposition from beta particles in oxygen is not correct. Such a picture predicts that increased pressure in the generator vessel results in increased ozone concentration in effluent gas until that pressure is reached at which all beta energy is expended within the generator gas (and none of the energy is lost in the vessel walls). Once the critical pressure has been exceeded, the simple picture then predicts a decrease in ozone concentration in effluent gas because of increased effluent flow (as

pressure increases). This is not observed.

Increase in ozone concentration from all orifices is observed until the pressure reaches 30 atmospheres (about 450 psig), after which, however, the concentration remains constant up to the highest pressures tested (100 atmospheres at BNL; 800 psig at RTI). This latter behavior seems to reflect a balancing of two effects; one, the predicted decrease in ozone concentration due to the increased flow rate through the generator; and two, an increase in ozone concentration due to shorter residence-time of produced-ozone in the radiation field where it can be destroyed (2). That these two effects just balance each other is fortuitous and could probably not have been calculated, because of the extreme complexity of the system (3, 4). There is some evidence that the concentration of ozone falls off slightly with increased pressure--a maximum occurs at about 550 psig -- but confirmation of the effect requires more time than was available for these experiments. This is discussed later.

The balancing of these two effects has a fortunate consequence, however. It is unneccessary to measure pressure--only be assured that it exceeds the critical pressure of about 30 atmospheres, or 450 psig. And it is not necessary to measure effluent flow rate-one only needs to be assured that enough gas is passing out of the generator to exceed the requirements of the instruments being calibrated.

D. Ozone Concentrations

Ozone concentrations were measured using an RTI-NAPCA chemiluminescent ozone meter. The calibration lamp in this instrument was recalibrated for these experiments by means of the neutral buffered KI method (7). Breathing-grade oxygen was dried by passing it through a dry-ice/acetone bath before passing it into the generator.

Initial experiments were conducted to determine the concentration of

ozone as a function of applied pressure. What was at first attributed to be irreproducibility in the system later proved to be an underestimate of time required to reach equilibrium. Only after several days at a given pressure is the maximum ozone concentration produced from orifice 1. Early experiments, therefore, are in error with respect to magnitude of ozone output, but on any given day the ozone concentrations are comparable one with another for the various pressures investigated. Thus, Table V shows ozone concentrations as a function of pressure for one day's experiments. These are different from the values found at a later date which are higher. Also, the low value at 500 psig was taken early in the day. Experiments made on other days show little difference in ozone concentration when operating at 450 psig and 550 psig. Because of the rapid consumption of gas by orifice 3, it was not investigated in detail. The ozone concentration from this orifice is about one third that from orifice 2, viz. 0.05 ppm.

TABLE V

Ozone Concentrations as Function of Oxygen Pressure

O_2, psig	O_3, ppm, Orifice 1	Orifice 2
500	0.42	0.14
550	0.47	0.15
650	0.48	0.15
750	0.46	0.15

Since it seemed apparent that nothing additional could be learned from measuring ozone concentrations over long periods of time at various pressures from 400 psig to 800 psig, one pressure, 500 psig, was chosen to study in detail. This is above the critical pressure and should be representative of ozone concentrations to be produced at all the other pressures.

There are two ways in which the ozone generator can be used; One is to pressurize the generator fresh each day, as if it were being carried to different installations for the purpose of calibrating stationary instruments. The other method is to set up the generator and keep it always at pressure (in these experiments, 500 psig) and bring instruments to the generator for calibration. The results are different.

To investigate the first method of operation, the generator was pressurized each day for two weeks, being let down to one atmosphere of dry oxygen each night. The method of pressurizing was found to be important. Since we used the dry-ice/acetone trap for removing water from the oxygen, it was found necessary to <u>slowly</u> apply pressure to the generator. When the reduction valve was manipulated rapidly, it was found previously that oxygen rushed through the trap so rapidly that it was not cooled thoroughly. The oxygen admitted to the generator, therefore, had much more than 0.3 ppm moisture content, with the resulting effect of low ozone concentrations being produced. The procedure adopted was one of increasing gradually the pressure to 500 psig over a period of four minutes. Relatively stable ozone production occurred within two or three hours of start-up, then. Table VI summarizes these experiments.

TABLE VI

Ozone Production from Periodic Pressurization of Generator

Day	O_3 Conc., ppm (500 psig)
1	0.264
2	0.326
3	0.327
4	0.360
5	0.406
6,7 (Weekend)	
8	0.382
9	0.400
10	0.421
11	0.429

Following this series of experiments, the generator was pressurized to 500 psig on a Monday morning and kept at that pressure until Friday night. Table VII summarizes these experiments.

TABLE VII

Ozone Production from Continuous Pressurization of Generator

Day	O_3 Conc. ppm (500 psig)
1	0.392
2	0.500
3	0.508
4	0.506
5	0.526

The conclusions are clear. It is not possible to use the generator intermittently as a source of ozone of known concentration. The generator must be set up and kept at a given pressure for several days before the ozone concentration achieves a reproducible value.

CONCLUSIONS AND RECOMMENDATIONS

The ozone generator using Sr-90 as an energy source produces ozone at a maximum concentration of about 0.50 ppm. A combination of physical and chemical phenomena occurring in the radiation field makes the ozone concentration from any given orifice independent of flow rate if pressure in the chamber exceeds 400 psig. Table VIII summarizes these concentration and flow-rate data. It is unfortunate that the ozone concentration is not

TABLE VIII

Summary of Flow Rate - Ozone Concentration Data

Orifice	O_3 Conc., ppm	Flow Rate ml/min (400-800 psig)
1	0.50	164 - 305
2	0.15	810 - 1800
3	0.05	7410 - 14000 (est.)

continuously variable from low values up to maximum. Maximum ozone concentration is obtained from orifice 1 only after several days operation at a fixed pressure (above 400 psig). Shorter times may produce maximum ozone from the other orifices.

The device should prove very useful if it is set up as a standard source of ozone and always kept in operation. To this purpose the following recommendations are made;

1. The generator should be set up in a permanent location with both inlet and outlet manifolds permanently attached.

2. Dry oxygen in tanks should be attached to the inlet manifold so that empty tanks may be replaced without reducing pressure on the generator. Dry oxygen should be purchased rather than drying oxygen by means of a dry-ice/acetone trap. The latter requires daily attention.

3. Orifice 2 will provide 1.1 liter per minute of about 0.15 ppm ozone if the generator is pressurized to 500 psig. This flow rate and ozone concentration should suffice for most needs of NAPCA. A higher pressure may be applied if greater flow rate is required, but this will then use correspondingly more oxygen. (The 1A cylinder contains approximately 6000 liters of gas initially at 2200 psig. About three days of continuous usage at 1.1 1/min will reduce the pressure to 500 psig).

4. The tube leading from the orifice to outlet manifold can be either teflon or stainless steel. This manifold (which may be attached permanently to the orifice, if desired) should be stainless steel or glass and possess at least 4 capped outlets to which can be attached the instruments to be calibrated.

5. It may be desirable to monitor continuously the outlet manifold flow rate. A flow meter, therefore, should be attached to one of the outlets and all others kept capped when not attached to the instruments.

6. An ozone concentration intermediate between 0.2 ppm and 0.5 ppm, and a corresponding flow rate between 190 ml/min and 1100 ml/min, can be obtained by reworking the design of orifice 4. As presently constructed, this orifice is unusable.

7. The ozone concentration from the generator should be monitored continuously over several months time using an RTI-NAPCA chemiluminescent ozone meter. Periodic calibration by means of the neutral buffered KI method should be made.

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A P P E N D I X

BNL 14199

Sr^{90} OZONE GENERATOR

For Sub-ppm Concentration Range

Model 1

Instruction Manual

Developed by

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SECTION 1

INTRODUCTION

1.1 PRINCIPAL OF OPERATION

Ozone can be produced by electric discharge, photolysis, and radiolysis, which is the method employed in the Sr^{90} Ozone Generator. The beta radiation emitted by the Sr^{90} is absorbed by oxygen with the subsequent production of excited states of oxygen molecules, atoms, and ions and the ultimate formation of ozone.

The Sr^{90} Ozone Generator was designed to produce ozone in the concentration range from approximately 0.002 to 0.6 parts per million (ppm) by volume of O_3 in O_2 to simulate the quantities found in the atmosphere. The advantages of the Sr^{90} Ozone Generator compared to electric discharge and photolysis units are:

1. No power - the Generator requires no electricity,
2. Long life - the half-life of the Sr^{90} is 28 years and is predictable,
3. Inherent low concentrations - eliminates dilution problems connected with electric discharge generators, and
4. Simplicity, ruggedness, portability - not present in other units.

1.2 GENERAL DESCRIPTION OF GENERATOR

1.2.1 Shipping Container

The container used for transportation of the Sr^{90} Ozone Generator is a standard Department of Transportation 6M Type B drum measuring approximately 16 x 22 in. high (cf. Figures 1 and 2). Concentrically within the drum is the 2R primary containment (6 x 14 in. high), which is surrounded by fiberboard discs and rings; the complete Generator is housed in the 2R container under the threaded cap.

1.2.2 Generator

The complete Sr^{90} Ozone Generator located at and below the bulkhead at the top of the 2R container (cf. Figure 3) consists of a 1/4 in. inlet and four-1/8-in.-outlet Swagelok connections, a rupture assembly (2,300 ± 50 psig), the Generator reaction vessel, and two filters (60 μ)--one before and one after the reaction vessel. The filters are provided to contain the Sr^{90} within the 2R containment in the unlikely event the source should rupture and the rupture assembly is to prevent accidental over-pressurization of the reaction vessel. All the tubing is 1/4 in. stainless steel with the exception of 1/8 in. tubing from the second filter to the fout outlet ports.

1.2.3 Reaction Vessel

The 2 1/2 in., schedule 40, stainless steel reaction vessel is shielded by 3/4 in. of lead and is contained within an approximated 4 1/4 in. diameter by 5 in. steel can (cf. Figure 4). Mounted axially within the vessel is a 1/16 in. diameter by 2 in., doubly encapsulated stainless steel "needle" containing 0.5 curies of Sr^{90} oxide beads (The 3M Company).

1.3 SPECIFICATIONS

Weight:	Total (as shipped), 109 lbs.
	Capped 2R container with Generator, 54 lbs.
Pressure:	Maximum operating, 1,500 psig; rupture disc will burst at 2,300 ± 50 psig; minimum rupture pressure (reaction vessel), 8,000 psig.
Temperature:	Ambient (24°C); unaffected by temperature from 18° to 30°C.
Gas:	USP O_2 (<0.4% N_2); dew point <-76°F (<10 ppm H_2O); a dryer should be used.

Flow range: 50 to 50,000 cc/min.

Ozone concentration: 0.002 to 0.6 ppm by volume.

1.4 RADIATION LEVELS (mr/hr)

	Maximum radiation level at		
	Top	Side	Bottom
Reaction vessel	5.0	12.0	4.0
In 2R container (cap off)	0.6	7.5	3.0
As shipped in 6M container	<0.1	1.2	0.9

SECTION 2

OPERATING INSTRUCTIONS

2.1 FLOW SYSTEM

The schematic flow diagram shown in Figure 3 indicates the way in which the Sr^{90} Ozone Generator is to be used. A cylinder of oxygen containing less than 10 ppm of H_2O is connected via a high pressure regulator (0 to 1,500 psig delivery pressure) to a dryer. This may be either a tube containing molecular sieve or a dry ice-acetone trap or both. The dried gas is then connected to the 1/4 in. inlet Swagelok fitting using 1/4 in. stainless steel tubing. Depending upon the ozone concentration desired, a 1/8 in. stainless steel line should be connected to one of the exit ports for delivery of the ozone to the point of use.

2.2 PARAMETERS AFFECTING OPERATION

The following information should be carefully studied to insure most accurate and comprehensive utilization of the Sr^{90} Ozone Generator. The important parameters affecting these low O_3 concentrations are flow rate, pressure, sample line material, moisture, and ozone conditioning of the clean lines.

2.2.1 Flow Rate

Since the ozone concentration at a given pressure is inversely proportional to the flow rate, it is important that each part agree within 5% of the values as given in Section 3.2.1. When changing from one port to another, allow 1 hour to obtain steady state conditions for orifice 1 and 10 minutes or less for the other orifices.

2.2.2 Pressure

In the range from 30 to 100 atm, the ozone concentration is nearly independent of pressure (cf. Section 3.3.4) and is not a significant variable. Below 30 atm (426 psig) the ozone concentration begins to decrease significantly; therefore, more precise measurement is required. The pressures referred to throughout this Manual are the delivery pressures as indicated by the regulator gauge on the O_2 supply tank. A Matheson Gas Products model 3 regulator with a delivery pressure range of 100 to 1,500 psig was used in the calibration.

2.2.3 Sample Line Material and Method of Cleaning

Stainless steel is the preferred material for both the trap, the 1/4 in. inlet tubing, and the 1/8 in. sampling lines (short lengths of polyethylene tubing are also satisfactory on the effluent stream). The tubing must be thoroughly clean and contain no traces of organic matter such as machining oils or drawing lubricants. It is best to clean all tubing with solvents and solutions in the following order: alcohol, aromatic (toluene), alcohol, alcoholic sodium hydroxide solution (12 g NaOH in 12 g H_2O diluted to 100 ml with methanol), alcohol, dilute nitric acid (10% HNO_3 in H_2O), water, acetone, toluene, and alcohol. By this method the last trace of any organic should be gone when the tubing is dried.

2.2.4 Moisture

Water vapor is known to catalyze the decomposition of ozone and, therefore, the extent of its pressure is extremely important. The data shown in Table I give a demonstration

TABLE I

Orifice 1, 50 atm O_2

H_2O, ppm	O_3, ppm
620 (sat.)	0.03
20	0.29
7	0.42
2	0.57
<1	0.60

of the effect of moisture on the ozone concentration from orifice 1 at 50 atm. The moisture content was determined using the CEC Moisture Monitor (cf. Section 4.3). Using O_2 saturated with water vapor reduces the ozone concentration nearly to zero; and even at 20 ppm of H_2O, the O_3 concentration is half that at 2 ppm of H_2O or less. Thus the moisture in the effluent stream must be less than 2 ppm.

2.2.5 Ozone Conditioning

Even after thorough cleaning and drying, a newly connected piece of tubing will decompose and remove a significant amount of ozone. For example, a 6 in. piece of 1/8 in. tubing, properly cleaned and dried, initially will reduce the ozone concentration from orifice 1 at 50 atm from 0.6 to approximately 0.4 ppm; only after 5 to 20 hours of continuous operation is the specified concentation attained. Therefore it is advisable that when connecting any new lines at least 24 hours be allowed for the tubing to equilibrate with the ozone atmosphere.

2.2.6 Ambient Temperature

Large deviations from normal ambient temperature should be avoided since the rate of decomposition of ozone

increases with increasing temperature and would necessarily give yields different from those given in the ozone calibration curves.

2.3 DETAILED OPERATING INSTRUCTIONS

2.3.1 Preliminary

Open the shipping drum, remove the top fiberboard disc and one ring, and carefully tip the shipping drum on its side (cf. Figure 1). Cautiously slide out the inner container (Note: This relatively small package weighs 54 pounds and is bottom-end heavy).

Grasping the lower end of the 2R container in a clamp or vise, remove the threaded cap using a large wrench. The connections to the Sr^{90} Ozone Generator are now visible and the Generator is now ready for the tubing connections.

2.3.2 Connections

The Generator inlet (1/4 in. Swagelok) and four outlet (1/8 in. Swagelok) connections have been capped with an atmosphere of dry (~1 ppm H_2O) O_2 within. It is advisable not to open either the inlet or outlet connection until just prior to hookup.

A stainless steel molecular sieve trap (30 cc volume of molecular sieve will sufficiently dry three standard-200-ft^3-cylinders of O_2 containing 20 ppm H_2O) or a U-tube of 1/4 in. stainless steel tubing immersed to a depth of 12 in. in dry ice-acetone (the latter is preferable because of the high gas velocities) should be connected as shown in Figure 3 (see Section 4.4). To this should be connected a 1/4 in. stainless steel tube which has been cleaned as per Section 2.2.3. With a low flow of oxygen established, heat the tube from the

trap to the end with a torch or hot air gun to remove the excess moisture from the walls of the tube before connecting to the Sr^{90} Ozone Generator. This should be done two or three times.

Now the tube may be connected to the 1/4 in. Swagelok fitting on the bulkhead while still maintaining a low flow of O_2. The necessary length of 1/8 in. stainless steel tubing should also be cleaned and dried to be connected later via one of the four orifices to your experimental apparatus downstream from the Sr^{90} Ozone Generator must be scrupulously clean; however moisture is not as critical after the ozone has been produced.

2.3.3 Preliminary Operations

Mount a calibrated flow meter on orifice 1, set the pressure on the O_2 regulator at 50 atm (720 psig), and compare the flow with that of Section 3.2.1. The flow should agree within 3 to 4% of that in the Table (Note: Make sure the gauge on the regulator is accurate). If the deviation is too large refer to Section 4.1.

Next, remove the flow meter and attach a short length of cleaned 1/8 in. stainless steel tubing to orifice 1, heat the tube to remove excess water, and connect to a 25 ml impinger using a short piece of polyethylene tubing. It is advisable to have maintained the gas flow at 300 to 400 cc/min through all of these changes. Now follow the procedure of Section 3.3 for determining ozone and continue to operate from orifice 1 at 40 to 50 atm until the ozone concentration reaches steady-state (~0.52 to 0.64 ppm). This may take from 1 to 3 days (see Section 4.5 if the ozone concentration at steady state is low).

Now connect the complete effluent tubing system which will run to the user's experimental apparatur and determine the ozone concentration until it again reaches steady state. This again may take from 1 to 3 days; the shorter the length of effluent tubing used, the quicker the ozone concentration will reach steady state.

2.3.4 Operation

If the previous steps have been carefully adhered to, actual operation of the Sr^{90} Ozone Generator will be simplified and the results should be quite reliable.

Having selected the proper orifice for the ozone concentration desired (cf. Figure 7), set the pressure regulator on the tank between 10 and 100 atm absolute (132 to 1,455 psig) to obtain the flow desired (cf. Figure 6). The time to achieve steady state should be about 1 hour for orifice 1 at any pressure and 10 minutes or less for the other orifices.

2.4 STANDBY OPERATION

If the Sr^{90} Ozone Generator is to be operated during the day only, it is best to switch to orifice 1 at low pressure (50 psig) for these short standby periods. This keeps the lines clean and conditioned by conserves gas (a dry ice-acetone trap will last overnight unattended). And steady state is quickly achieved at the new conditions in the morning.

For longer periods of shutdown, simply cap the exit line. If a dry ice-acetone trap has been used, this must be disconnected from the Generator prior to warming to room temperature. When the Generator has not been used for more than 1 week, it is advisable to start with the Preliminary Operations (Section 2.3.3).

SECTION 3

CALIBRATION

3.1 FLOW CONTROL SYSTEM

There are four exit ports (1/8 in. Swagelok) on the bulkhead of the 2R container; they are connected by tee-fittings to the filter on the outlet side of the reaction vessel (cf. Figure 3). An orifice has been incorporated into ports 1, 2, and 3 (port 4 has unrestricted 1/8 in. tubing) at the exit side of their respective Swagelok tees (below the bulkhead) such that port 1 has the lowest flow and port 4 has the highest. Calibration of the flow rates achieved by these ports is given in Section 3.2.1.

3.1.1 Orifice Design

The simplest method for producing low flow rates at high pressure drops is shown in Figure 5. An approximately 3/8 in. long x 1/16 in. diameter stainless steel rod is inserted in the end of the 1/8 in. o.d. x 1/16 in. i.d. stainless steel tubing which is connected to each bulkhead port (the rods are in the ends within the tees with the caps dyed red). A different sized flat has been cut on each rod; e.g., about half the cross sectional area of the rod was removed for port 3, about one-tenth for port 2, and only about 0.2% for port 1. Because of the extremely small cross sectional area for flow in port 1, a 5 μ stainless steel frit has been placed in the inlet side of the tee containing this port. The rods are held in place by the swaging action of the fittings.

By this method, for example, a pressure of 50 atm (720 psig) on the delivery pressure gauge is reduced to atmospheric pressure at a flow rate of 395 cc/min through port 1. The other ports were designed to deliver flow rates approximately

6 to 7 times the preceding one. The procedure involved cutting a flat, swaging a minimal amount to assure leaktight connection, and then further swaging to adjust the flow to the desired rate. The flow rate is determined predominently by the size of the flat and only a small amount of adjustment is available by loosening or tightening the Swagelok.

3.2 FLOW MEASUREMENT

Four predictability flow meters (Manostat Corp.) were used to determine the O_2 flow rates from 50 to 50,000 cc/min. A knowledge of the flow is not essential to normal operation, but there are two cases for which a flow rate must be determined--in determining O_3 concentrations by the iodometric method and when checking the calibration of the orifices.

3.2.1 Flow Rate Check Points

Since for a fixed pressure, the ozone concentration is precisely inversely proportional to the flow rate, it is essential that the flow through each port agree with the values below:

P = 50 atm (720 psig)

Port No.	1	2	3	4
Flow, std* cc/min	395	2,450	14,500	60,000

*std is 0°C and 1 atm.

Reproducibility of these results has been found to be about 3%. The complete flow data is given in Figure 6 for orifice 1; the other ports are multiples thereof.

3.3 OZONE DETERMINATION

The method of determining the concentration of ozone in the effluent streams is essentially that as described by Saltzman

(Neutral Buffered-Potassium Iodide Method, Selected Methods of the Interbranch Chemical Advisory Committee) in which ozone liberates free iodine by oxidation of the iodide and the iodine is determined colorimetrically. The only change made was the use of starch as an indicator--with the starch it made no difference whether the sample was analyzed 5 min or 1 1/2 hr after being collected. Comparison with an Ozone Meter (Mast Development Corp.) in the range of 0.05 to 0.6 ppm O_3 indicated that the meter was reading approximately one-half the absolute iodometric method.

3.3.1 Procedure

A 10 ml aliquot of the neutral buffered-potassium iodide (13.61 g KH_2PO_4, 14.2 g Na_2HPO_4, 10.0 g KI in 1 liter) was placed in a 25 ml gas impinger and a sample stream from the Sr^{90} Ozone Generator of about 350 cc/min was passed through the solution for a time necessary to achieve an iodine concentration of from 1.5 to 6 ppm. To this was added 1 ml of concentrated starch solution (Acculute iodometric starch indicator concentrate diluted to 100 ml instead of 1,000 ml) and the color was measured at 440 mμ with a Delta Water Analyzer.

3.3.2 Accuracy of Determination

There are two important factors which limit the accuracy of the ozone determination by this method--the limit of detection of iodine and the efficiency of sampling.

The ozone concentration in the gas stream is calculated from the equation

$$C(O_3) = \frac{88.4\ (V)\ C_I}{F\ t}$$

where:

V = Volume of iodide solution used, ml,

C_I = concentration of iodine, ppm by wt,

F = flow rate of sample, cc/min, and

t = time of sampling, min.

The smallest practical volume of iodide solution that can be used is 10 ml, the smallest concentration of iodine measurable to within 20% is 0.5 ppm, and the largest flow possible with less than a 15% loss of ozone through the bubbler is about 350 cc/min. Thus, 2 hours would be required to detect 0.01 ppm O_3 in O_2.

3.3.3 Efficiency of Sampling

The flow rate of the sample and the concentration of ozone strongly effect the sampling efficiency. The length of sampling time, the volume of iodide solution, and the concentration of iodine attained in the bubbler seem to have a negligible effect. Concentrations as high as 11 ppm I gave the same calculated concentration of O_3 as when the sample was collected for 1/10 the time (1.1 ppm I). About 10 to 15% of the ozone passed unreacted to a second bubbler when the concentration of O_3 was 0.6 ppm and the flow rate was 350 cc/min. At the same flow rate but at an O_3 concentration of about 0.1 ppm, the "loss" was 15 to 20%. And at 1,500 cc/min and 0.1 ppm, the "loss" was 25 to 30%.

3.3.4 Ozone Calibration Curves

Of the four outlet ports, complete data was obtained at the two ports which gave the highest ozone concentrations (1 and 2). As shown in Figure 7, the ozone concentration decreases only slightly for a particular orifice when decreasing the pressure from 100 atm to about 30 atm, below which the

concentration drops more rapidly. The ratio of ozone concentration for ports 1 and 2 at the same pressure was found to be exactly inversely proportional to the ratio of the respective flow rates. This observation was used to determine the curves for ports 3 and 4. It can be seen that 2 experimental points for orifice 3 fall on the predicted curve for that port. The concentration of ozone from port 4 was too low to determine experimentally be the iodide method.

SECTION 4

MAINTENANCE AND TROUBLESHOOTING

4.1 FLOW ADJUSTMENT

The greatest care has been taken to exclude foreign matter from the area of the orifices including the installation of a 5 μ filter in line before orifices 1 and 2. However, the possibility does exist that over a period of time enough fine material may accumulate in orifice 1 decreasing the flow and necessitating an adjustment (it is unlikely that ports 2, 3, or 4 will become restricted).

Thus, it is essential that the flow from the orifices be compared occasionally with the check points as found in Section 3.2.1. Deviations up to 20% can possibly be corrected by tightening or loosening the fitting containing the orifice (Swagelok cap dyed red). Check to make sure that the adjustment has not caused a leak.

If a simple adjustment cannot be made, remove the line containing the orifice rod, pull out the rod, and clean with acetone or alcohol. Reinstall and adjust flow as above. Operation for 24 hours will probably be necessary to achieve the original O_3 concentration.

4.2 FILTERS

The two 60 μ filters should not need any attention as long as clean oxygen is used as the supply gas. The 5 μ filter (cf. Section 3.1.1) might, over an extended period of time, become clogged with fine particulates thus decreasing the flow through orifices 1 and 2. Cleaning should be accomplished by removing the Swagelok tee containing the two orifices and filter, back-flushing with solvent, and drying.

4.3 MOISTURE DETERMINATION

If O_2 containing less than 10 ppm H_2O and a dryer (molecular sieve or dry ice-acetone) are used, there should be no problem from moisture contamination. Thus each O_2 tank should be analyzed for moisture prior to use and the efficiency of the drying technique should be checked using an instrument such as the CEC Moisture Monitor, Type 26-303. The dried gas should contain less than 2 ppm H_2O. Note: If a dry ice-acetone trap is used, the moisture content must necessarily be less than 1 ppm and no determination need be made.

4.4 MOISTURE TRAPS

A 30 cc molecular sieve moisture trap is sufficient for 3 tanks of O_3 when the H_2O content of the tank O_2 is less than 10 ppm. The molecular sieve is best regenerated by evacuating overnight (through a minimum opening of 1/4 in. tubing) at 400° to 425°C and then for 1 hour at 300 to 400 cc/min of dry nitrogen. Cool the trap, purge with O_2, and reconnect to the system.

If the moisture content of the cylinder O_2 is 10 ppm or greater, it is advisable to use the dry ice-acetone trap described in Section 2.3.2. This trap is also preferable if most of the work is performed at the higher flow rates (orifices 3 and 4). Disconnect the trap from the Sr^{90} Ozone Generator before warming it to room temperature and reheat the 1/4 in. inlet line after cooling the trap but before connecting to the inlet.

4.4.1 Excess Moisture in Generator

Occasionally it will not be possible to obtain less than 2 ppm H_2O in the effluent even with proper drying because of excess moisture on the walls of the Generator from earlier

sources. This "tramp" moisture will eventually be removed by continuous operation with properly dried O_2; the time necessary to obtain the proper conditions will, of course, vary with the amount of moisture in the Generator. Raising the temperature (as high as 100°C without damage to the Generator) and/or evacuating will speed the drying; but additional time will still be necessary for the walls to reach a steady state ozone concentration. Use the procedure in Preliminary Operations (cf. Section 2.3.3) to establish the proper conditions.

4.5 TROUBLE SHOOTING

Having a thorough knowledge of the Sr^{90} Ozone Generator, its theory of operation, its capabilities and limitations, is basic to eliminating problems. The following Table lists several of the common troubles.

Symptom	Possible Cause	Action
1. Low steady state ozone concentration (after 3 days of operation).	Orifice flow has increased	Check flow rate and adjust (cf. Section 4.1)
	Effluent line not clean	Compare with another line or clean line (cf. Section 2.2.3)
	Leak in effluent line (if determining ozone with impinger)	Cap line and check for lack of pressure build-up; repair leak
	Moisture content too high	Analyze effluent (cf. Section 4.3); see Symptom 3
	Internal leak	Pressure leak-test entire Generator

Symptom	Possible Cause	Action
2. High steady state ozone concentration	Orifice flow has decreased	Check flow rate and adjust (cf. Section 4.1)
	Pressure higher than reading (only below 30 atm)	Check pressure gauge accuracy
3. Moisture content high (>2 ppm from Generator)	O_2 not sufficiently dried	Switch to dry ice-acetone trap or regenerate molecular sieve (cf. Section 4.4)
	Excess moisture from previously improperly dried O_2	Dry the Generator (cf. Section 4.4.1)
4. Flow incorrect	Pressure not set properly	Check pressure gauge accuracy
	Orifice characteristic has changed	Adjust orifice (cf. Section 4.1)

FIGURE 1

FIGURE 2

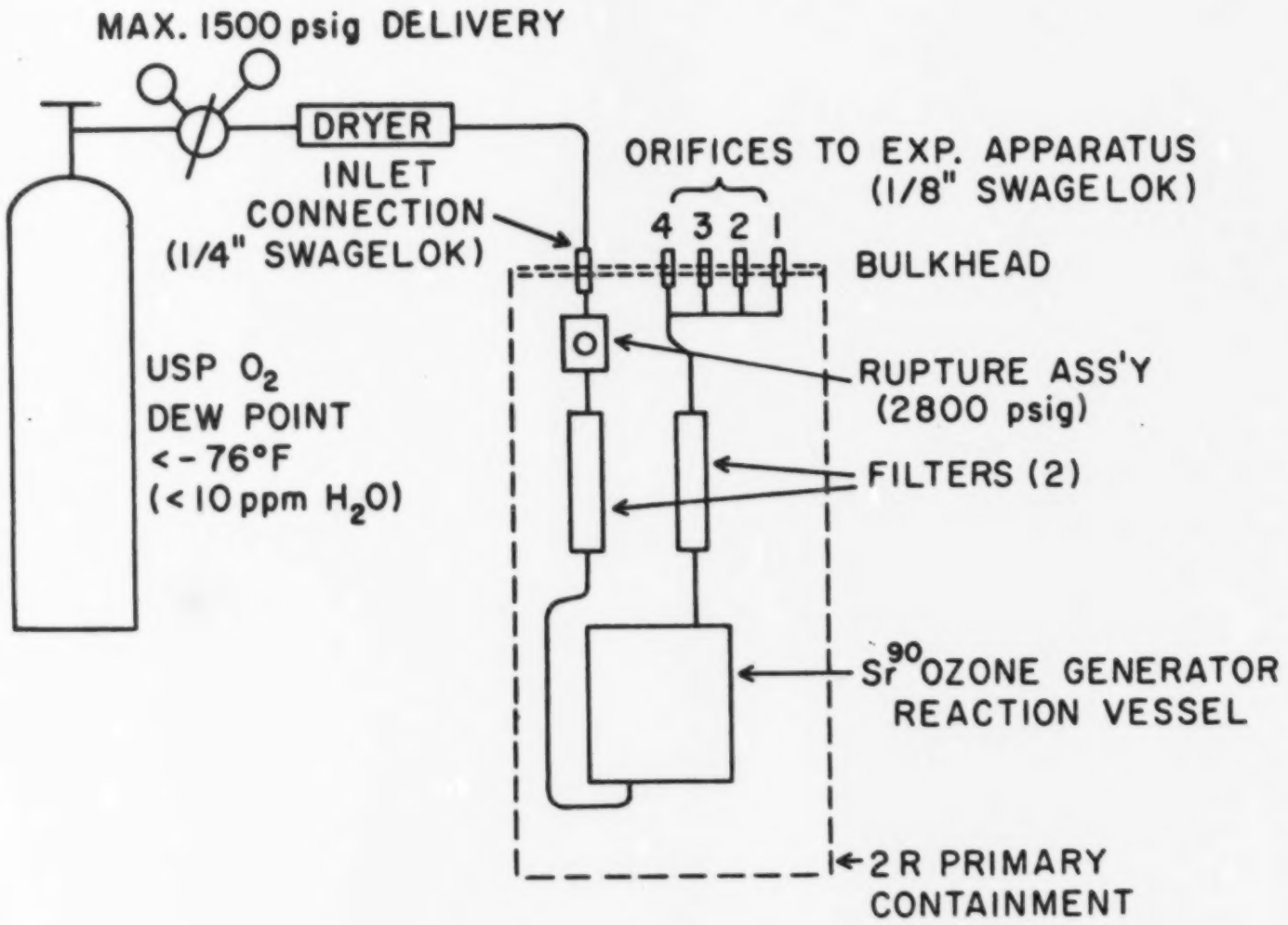
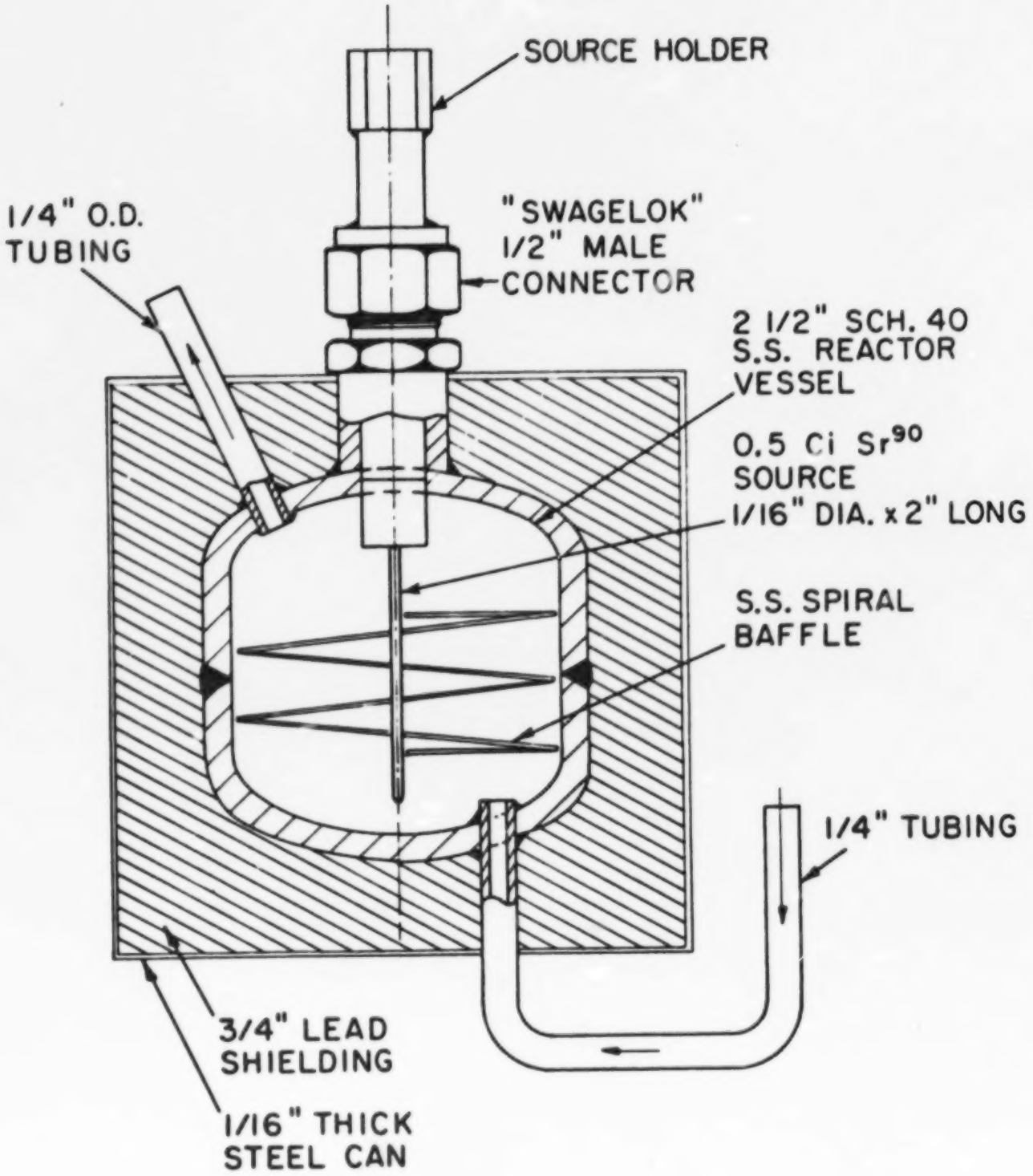


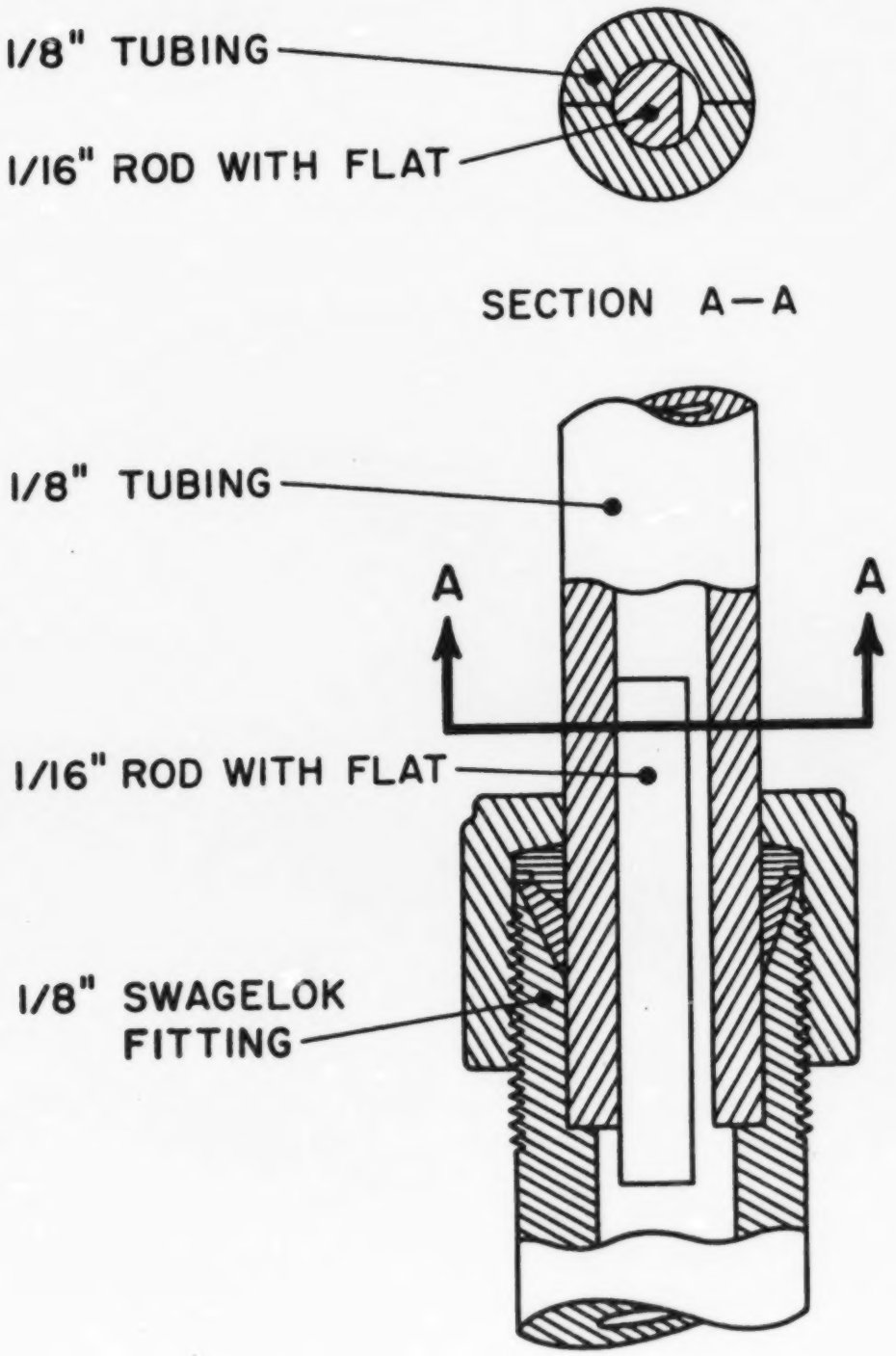
Figure 3

SCHEMATIC FLOW DIAGRAM OF Sr^{90} OZONE GENERATOR



Sr^{90} OZONE GENERATOR REACTION VESSEL

Figure 4



ORIFICE DESIGN

Figure 5

OXYGEN FLOW RATE = FLOW READING x ORIFICE MULTIPLIER

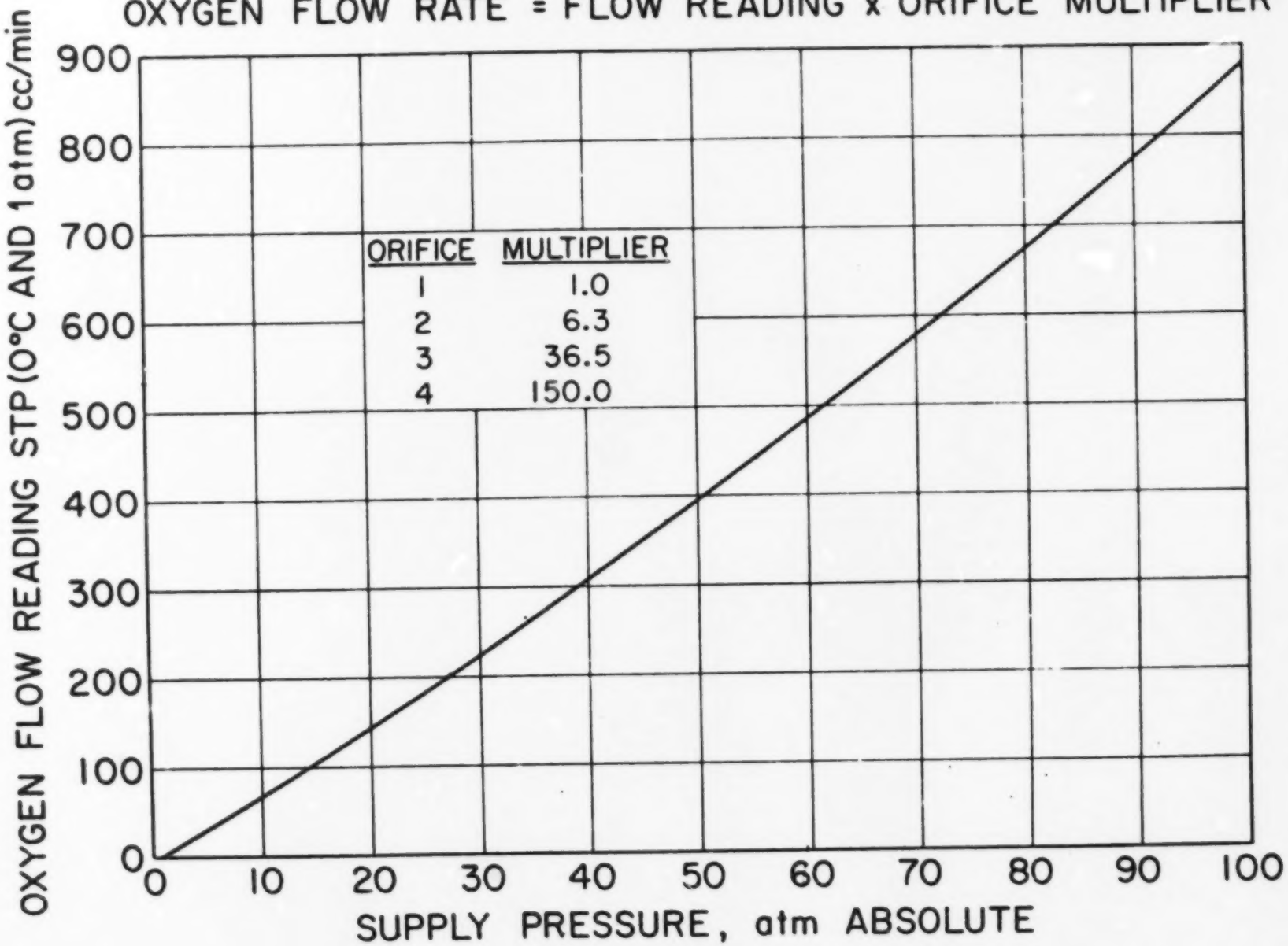


Figure 6 —

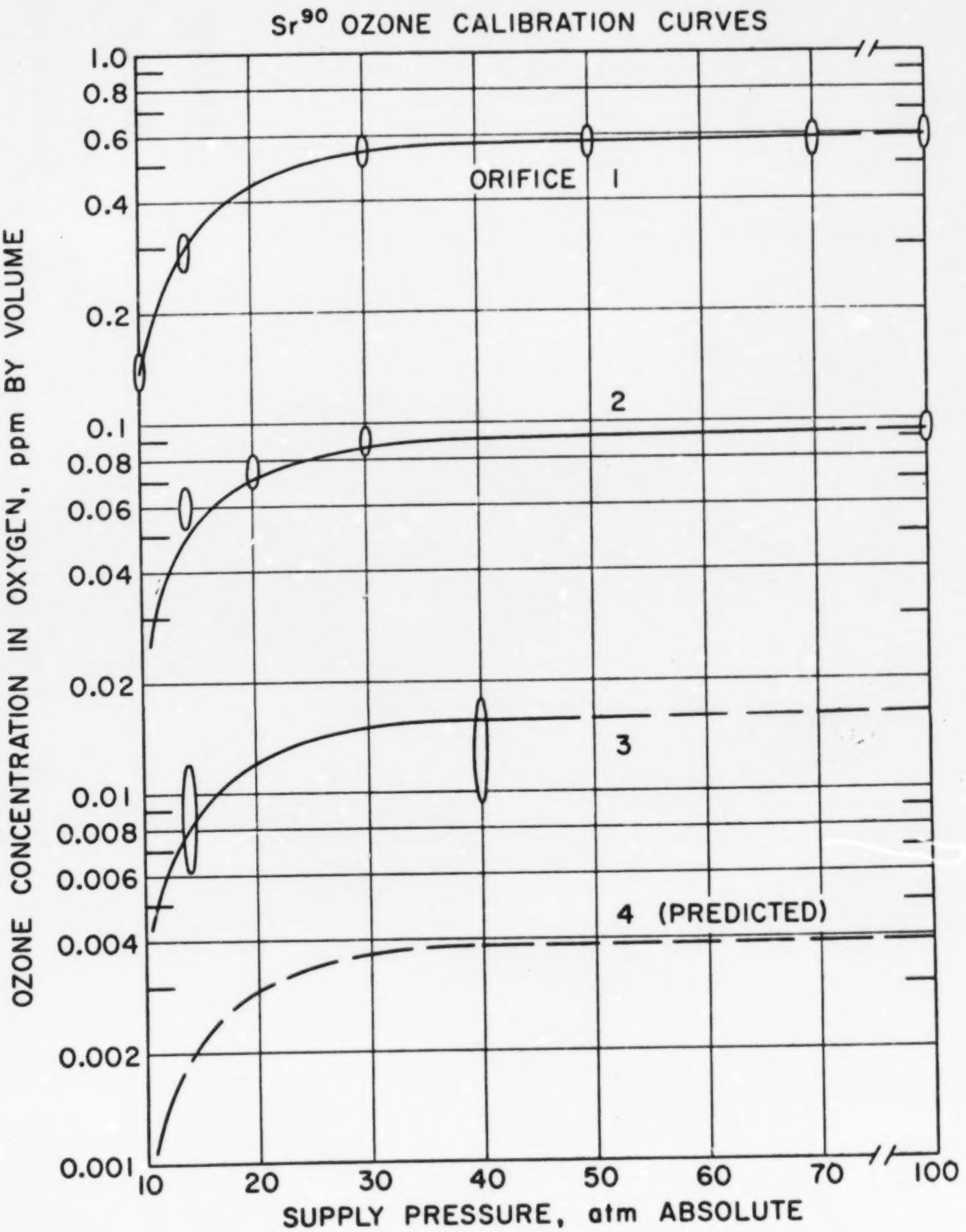

Sr90 OZONE CALIBRATION CURVES
OZONE CONCENTRATION IN OXYGEN, ppm BY VOLUME
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.002
0.001
ORIFICE 1
2
3
4 (PREDICTED)
10
20
30
40
50
60
70
100
SUPPLY PRESSURE, atm ABSOLUTE

Figure 7